1. HEXAARYLETHANES CONTAINING NAPHTHALENE AND ANTHRACENE GROUPS

2. THE STRUCTURE OF POLYPENTYNESULFONE

BY

JOHN WILLIAM SHACKLETON

B.A., Vanderbilt University, 1932

M.S., Vanderbilt University, 1933

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. HEXAARYLETHANES CONTAINING NAPHTHALENE AND ANTHRACENE GROUPS

INTRODUCTION

No single theory has yet satisfactorily explained the dissociation of hexaarylethanes to give triarylmethyl radicals. The preparation of the naphthyl substituted ethanes was undertaken to test the applicability of some of these theories, especially those concerning resonance[1] and steric hindrance.

DISCUSSION OF RESULTS

A study of the dissociation by the magnetic susceptibility method,[2] of the β-naphthyl series of ethanes compares well with other results on similar series. Dissociation of these substances in 0.1 molar solution and at 25°C are: di-β-naphthyltetraphenylethane (7-9%),[3] tetra-β-naphthyldiphenylethane (13%), and hexa-β-naphthylethane (above 60%—an estimation). Di-α-naphthyltetraphenylethane is dissociated to the extent of 27% at 0.1 molar concentration and 25°C. Di-α-naphthylphenylcarbinol has been prepared and is available for the preparation of the second ethane of this series. From evidence obtained, the tri-α-naphthyl compounds do not exist, due to loss of hydrogen to form dinaphthylene derivatives.[4] Di-α-naphthyldiphenyldibiphenylethane is 54% dissociated at the above temperature and concentration. β-Napthylphenylbiphenylcarbinol and the corresponding triarylmethyl chloride have not been obtained in crystalline form.

It is suggested that dissociation of these ethanes is principally a function of steric hindrance and resonance forces, supplemented by minor effects. Symmetry within the radical, itself, appears to account for the exaggerated increase in the dissociation of ethanes containing six similar groups over that observed in the case of the forms substituted with two or four dissimilar groups. This concept may not be carried too far, however. A preponderance of one of the three effects may mask the influence of one or both of the others.

Di-β-naphthylphenylmethyl chloride and tetra-β-naphthyldiphenylethane have not been reported previously. There have been no measurements reported for the dissociation of tetra-α-naphthyldiphenylethane, or for hexa-β-naphthylethane.

Preliminary investigations have been carried out on the starting materials necessary for the preparation of anthracene substituted free radicals.

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II. THE STRUCTURE OF POLYPENTYNESULFONE

INTRODUCTION

Pyrolysis of polypentynesulfone yields a compound, $C_{10}H_{16}SO_2$, which has been postulated as being a di-n-propylthiophene 1, 1-dioxide.[1] Confirmation of this structure and proper assignment of the position of the propyl groups should give valuable data on the structure of the original polymer. This was the aim of these investigations.

DISCUSSION OF RESULTS

Two of the three probable reduction products of $C_{10}H_{16}SO_2$ have been made previously.[2] A synthesis is proposed for the remaining one: 2, 4-di-n-propyltetrahydrothiophene 1, 1-dioxide. This involves the reaction of amylenehalohydrin-1, 2, or amylene oxide-1,2 with diethyl n-propylsodiomalonate to give a disubstituted ester, which, on saponification and acidification, followed by the loss of carbon dioxide and water, yields α, γ-di-n-propylbutyro-γ-lactone. This compound has been prepared.

Reduction of similar lactones has been shown to result in the formation of substituted tetrahydrofuranes and glycols.[3] Either product should be converted to the corresponding dibromide on treatment with dry hydrogen bromide. From this point the proposed reactions follow the course set forth in the preparation of the other two isomers; i.e., reaction of the dibromide with sodium sulfide and oxidation of the product with hydrogen peroxide.

Reduction of $C_{10}H_{16}SO_2$ has, thus far, given no products which can be correlated with known compounds. Attempts to dehydrogenate the substituted tetrahydrothiophene dioxides already available by bromination and subsequent dehydrohalogenation have not been successful.

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VITA

The writer was born in Louisville, Kentucky, on October 2, 1910. He attended the public schools of that city and, after two years in Louisville Male High School, transferred to Ogden Preparatory School at Bowling Green, Kentucky, where he graduated in June, 1927. He attended the Bowling Green Business University for one year, Western Kentucky Teachers College for two years, and transferred to Vanderbilt University in the fall of 1930. Here he received the degree of Bachelor of Arts in 1932 and the degree of Master of Science in 1933. From the fall of 1932 until May, 1935, he held teaching assistantships at Vanderbilt University. From May, 1935, until May, 1937, he was employed as a research chemist by the E. I. du Pont de Nemours and Company. In June, 1937, he entered the University of Illinois where he has held appointments as assistant in chemistry for the years 1937 to 1941.

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